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# An *ab initio* study of the $C_3^+$ cation using multireference methods

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## Abstract

The energy difference between the linear  $^2\Sigma_u^+$  and cyclic  $^2B_2$  structures of  $C_3^+$  has been investigated using large  $[5s3p2d1f]$  basis sets and multireference electron correlation treatments, including complete active space SCF (CASSCF), multireference CI (MRCI), and averaged coupled-pair functional (ACPF) methods, as well as the single-reference quadratic configuration interaction (QCISD(T)) method. Our best estimate, including a correction for basis set incompleteness, is that the linear form lies above the cyclic form by  $5.2_{-1.0}^{+1.5}$  kcal/mol. The  $^2\Sigma_u^+$  state is probably not a transition state, but a local minimum. Reliable computation of the cyclic/linear energy difference in  $C_3^+$  is extremely demanding of the electron correlation treatment used: of the single-reference methods previously considered, CCSD(T) and QCISD(T) perform best. The MRCI+Q(0.01)/ $[4s2p1d]$  energy separation of 1.68 kcal/mol should provide a comparison standard for other electron correlation methods applied to this system.

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# 1 Introduction

Over the last few decades, carbon clusters have aroused considerable interest both theoretically and experimentally; the review by Weltner and Van Zee<sup>1</sup> extends up to April 1989. A brief update of that review may be found in the introduction to Ref. 2; as a result of these latest developments, linear carbon clusters  $C_3$ ,  $C_4$ ,  $C_5$ ,  $C_6$ ,  $C_7$ , and  $C_9$  have so far been characterized.

The situation is less clear for the ions than for the neutral clusters. The "building block" of the ions is believed to be  $C_3^+$ ,<sup>3</sup> although its geometrical structure is not currently known. Older theoretical studies always assumed a linear structure (see, e.g., Ref. 4) by analogy with the neutral species.

The Coulomb explosion<sup>5</sup> experiments of Faibis *et al.*<sup>6</sup> at first sight appeared to indicate unambiguously that the structure was cyclic: preliminary *ab initio* calculations by Raghavachari (private communication quoted in Ref. 6) corroborated this conclusion. However, Vager and Kanter<sup>7</sup> remarked that the experimental intensity distribution of Faibis *et al.* could also be rationalized by assuming a linear structure with large amplitude bendings similar to those of neutral  $C_3$ ,<sup>8</sup> combined with a fairly high Boltzmann temperature of about 450 K. It therefore seemed desirable to perform an *ab initio* study to settle the issue.

Three such studies were performed independently, by Grev *et al.* (GAS)<sup>9</sup>, Raghavachari<sup>10</sup>, and Martin *et al.* (MFG)<sup>11</sup>. GAS used various configuration-interaction methods, including single, double, triple, and quadruple excitations (CISDTQ) in some cases, as well as full CI in the valence orbital space. They predicted a fairly large energy separation ( $\Delta E$ , positive sign favoring the cyclic form throughout this paper) of  $7 \pm 4$  kcal/mol using a combination of 11/35 CISDTQ (the notation signifying 11 electrons correlated in 35 orbitals), 11/12 full CI, and 11/45 CISD, all in the Huzinaga-Dunning double zeta plus polarization (DZP) basis set<sup>12, 13</sup>. However, GAS have recently published substantially revised data as an erratum<sup>14</sup>, in which they propose a barrier of  $4 \pm 4$  kcal/mol, i.e., that it is still an open question whether  $C_3^+$  is cyclic.

Raghavachari and MFG used more or less comparable theoretical methods, namely the 6-311+G(2df) basis set<sup>15</sup> and the recently proposed QCISD(T) method<sup>16</sup>, which can be viewed a good approximation<sup>17</sup> to CCSD(T)<sup>18</sup>, i.e., coupled cluster with all single and double excitations and a quasiperturbative account of connected triples. For technical reasons, MFG used additivity approximations at the CCD(ST) level<sup>19</sup> for assessing the effects of diffuse and additional polarization functions. The main difference

between these two papers is the choice of reference geometry, which was determined at the QCISD(T)/6-31G\* level by Raghavachari and at the MP2/6-311G\* level by MFG.

Raghavachari found a barrier of 3 kcal/mol at the QCISD(T)/6-311+G(2df) level from QCISD(T)/6-31G\* geometries, but considered his results unreliable as he found that the bending potential of the cyclic form went through a maximum around 100 degrees at the QCISD(T)/6-31G\* level. He then concluded that the QCISD(T) method artificially favored the linear form and that the barrier would be larger, in agreement with the original GAS value of  $7 \pm 4$  kcal/mol.

Unaware of the other work, MFG proposed a "best estimate" for the barrier of 2 kcal/mol on the basis of their calculations. Such a barrier height would indicate that the ion is on the borderline of quasilinearity.

More recently, Scuseria<sup>20</sup> has also investigated the structure of  $C_3^+$ , using a newly developed open-shell CCSD(T) code that uses a restricted Hartree-Fock (RHF) reference configuration. In similar basis sets to those used by Raghavachari and MFG, the CCSD(T) method yields results similar to those from QCISD(T). However, Scuseria has also investigated the use of much larger basis sets than these authors, up to [5s4p3d2f1g] atomic natural orbital (ANO) sets<sup>21</sup>. The basis set effects are very substantial, increasing the separation to 6.8 kcal/mol in the largest basis set. One consequence of this work is that it can be regarded as definitively established that basis set extension and, by implication, dynamical correlation, favors the cyclic form of  $C_3^+$ .

One significant limitation of all the results quoted so far is that they were obtained with single reference configuration wave functions. GAS actually performed CASSCF<sup>22</sup> calculations of the energy separation, obtaining 2.2 kcal/mol with a triple zeta basis set with two sets of polarization functions (TZ2P), but regarded their CI results as more reliable. The rather low energy separation at the CASSCF level suggests that non-dynamical (near-degeneracy) correlation effects favor the linear state, and that it may be crucial to obtain a balanced description of non-dynamical and dynamical correlation effects to predict a reliable separation. It therefore seems imperative to investigate the separation with a multireference method. In the present work we apply the CASSCF/MRCI and ACPF methods to the energy separation. Our computational methods are described in the next section, followed by our results and discussion. These are divided into three subsections, calibration of the  $n$ -particle space (correlation treatment), calibration of the one-particle basis, and identification of the linear geometry as a local minimum or a transition state. Our conclusions are given in Sec. 4.

## 2 Computational methods

Two basis sets were employed throughout the present work. The first is the DZP set used by GAS, and consists of Dunning's [4s2p] contraction<sup>13</sup> of the Huzinaga (9s5p) primitive set<sup>12</sup>, supplemented by a single six-membered *d* function with exponent 0.75. The second basis set considered was a [5s3p2d1f] basis set constructed from Dunning's [5s3p] contraction<sup>23</sup> of Huzinaga's (10s6p) primitive set<sup>12</sup>, supplemented by two sets of pure *d* and one set of pure *f* functions. The polarization exponents were optimized at the MP4(DQ) level for the C atomic ground state, and are given as:  $\alpha_d = 0.549$ ,  $\alpha_f = 0.775$ . The *d* exponent was split using the 'even scaling rule'  $\alpha/2$  and  $2\alpha$ . In some calculations, as noted in Sec. 3, an *f* exponent of 0.966 was used. This has little or no effect on the computed energy separations.

The CASSCF calculations all employed an active space comprising the 2s and 2p orbitals and electrons, that is, 11 electrons in 12 active orbitals. This generates very large CASSCF configuration spaces, on the order of 85 000 configuration state functions (CSFs), mandating the selection of reference occupations for the MRCI and ACPF calculations in order to keep the expansion lengths manageable. Reference occupations were included if any one of their component spin-couplings had a coefficient larger than some threshold in the CASSCF wave function. The thresholds ranged from 0.05 down to 0.01 and are discussed in more detail in the next section. Selection was carried out at both cyclic and linear geometries and the reference lists were merged for the MRCI and ACPF calculations. The C 1s electrons were not correlated in any calculations.

One complication with obtaining molecular orbitals (MOs) for calculations on the ground state of  $C_3^+$  arises from symmetry considerations. The cyclic  ${}^2B_2$  state can be viewed as one component of a Jahn-Teller distorted  ${}^2E'$  ( $D_{3h}$ ) equilateral triangle geometry. However, MOs optimized for the  ${}^2B_2$  state will not display  $D_{3h}$  symmetry and equivalence at an equilateral triangle geometry, and the CASSCF Hamiltonian matrix will not have degenerate lowest eigenvalues. In order to ensure that the MOs have  $D_{3h}$  symmetry properties at  $D_{3h}$  geometries, the MOs can be obtained from a  $C_{2v}$  calculation in which the lowest roots of  ${}^2B_2$  and  ${}^2A_1$  symmetry are averaged<sup>24</sup>. However, while the  ${}^2B_2$  state correlates with the nondegenerate  ${}^2\Sigma_u^+$  state of linear  $C_3^+$ , the  ${}^2A_1$  state correlates with one component of a  $\Pi$  state. Another  ${}^2B_2$  root ( $C_{2v}$  symmetry) must then be included to ensure  $D_{\infty h}$  symmetry MOs at  $D_{\infty h}$  symmetry geometries. Hence to obtain MOs that display full symmetry and equivalence properties at all geometries considered it is necessary to include three roots in a state-averaged CASSCF calculation. This was

done in all calculations in the present work in which MOs for a subsequent MRCI were being optimized. Calculations to determine CASSCF level vibrational frequencies were based on a single root CASSCF.

CASSCF, MRCI and ACPF energy calculations were performed using the MOLECULE-SWEDEN program system <sup>25</sup> running on the NASA Ames Central Computing Facility CRAY Y-MP/832 and NAS Facility CRAY Y-MP/8128. CASSCF vibrational frequencies were determined using the SIRIUS/ABACUS program system running on the NASA Ames Computational Chemistry Branch CONVEX C-210 and an IBM RISC 6000 model 530 workstation on loan from IBM Corporation.

The calculations at the LUC were performed using GAUSSIAN 88 <sup>26</sup> running on the IBM 3090/400e VF at the University of Leuven.

### 3 Results and discussion

#### 3.1 Calibration of the $n$ -particle space

Results using single-reference methods and the  $[4s2p1d]$  basis set are presented in Table I. As GAS considered the behavior of the computed  $\Delta E$  as a function of the number of virtual orbitals, we have done the same at the QCISD and QCISD(T) levels. The GAS "full CI" result is actually a full valence CI, performed in same MO space as the CASSCF results discussed below, so it has limited value as a benchmark for dynamical correlation treatments.

The most striking feature of the results of Table I is the extreme variation of  $\Delta E$  with the electron correlation method. Triple excitations have an especially large effect. The MP4 method breaks down completely, which illustrates the importance of higher-order effects. The reason for this is readily seen from Table II; the molecule does indeed exhibit exceptional multireference character. (For comparison with these figures, we note that the RHF configuration comprises less than 87% of the CISD wave functions computed by GAS.) As a further illustration, the computed CISD  $\Delta E$  changes by 5.5 kcal/mol depending on which size-consistency correction formula (Davidson <sup>27</sup>, renormalized Davidson <sup>28</sup>, Davidson-Silver <sup>29</sup>, or Pople <sup>30</sup> correction) is applied to the results. As this scatter in the results is of the same order of magnitude as the quantity to be computed, the use of CISD+Q results in investigating basis set expansion and basis set additivity corrections is questionable.

When comparing the QCISD(T) and full CI results of Table I, it should be recalled that the former are computed from a UHF, and the latter from an RHF reference wave

function. The difference between the GAS CISD results and our UHF-CISD calculation (denoted UCISD in Table I) can be used as an approximate correction: it suggests that the computed QCISD(T)  $\Delta E$  should be raised by approximately 1.59 kcal/mol to bring it on the same scale as the RHF-based calculations, leading to an approximate "RHF-QCISD(T)" result of -0.94 kcal/mol. This is in excellent agreement with the 11/12 full CI value of -1.02 kcal/mol.

As the virtual orbital space increases in size, the CISDTQ and QCISD(T) results diverge from each other. The rather large difference of 3.75 kcal/mol with 35 MOs may be caused by the following deficiencies of QCISD(T) with respect to CISDTQ; neglect of higher-order terms in  $\hat{T}_1$ , neglect of diagrams involving more than one connected triply-excited intermediate state, and neglect of connected quadruple excitations. On the other hand, CISDTQ is not, in general, size-consistent, and given the very large effect of size-consistency corrections on the CISD results, and the extreme multireference character, it is not at all clear a priori that unlinked diagrams involving quintuple and higher excitations (which enter at sixth order in MBPT) can be neglected.

The QCISD(T) method in the full 45 MOs, corrected with the 12 MO QCISD(T)/full CI difference would give an estimated  $\Delta E$  of 2.38 kcal/mol; the CISDTQ method in 35 MOs corrected with the 12 MO CISDTQ/full CI difference plus an estimate of the extension from 35 to 45 MOs from the Davidson-corrected CISD result yields an estimated  $\Delta E$  of 4.25 kcal/mol. The difference between these estimates is still on the order of magnitude of  $\Delta E$  itself.

The logical step is then to consider multireference methods. Both MRCI and averaged coupled-pair functional (ACPF)<sup>31</sup> were considered. The latter is approximately size extensive; to the former, a multireference analog<sup>32</sup> of the Davidson correction was applied. (These energies are denoted MRCI+Q.) CASSCF results are also included as these allow us to distinguish between internal and external correlation effects. All results are given in Table II.

A first set of calculations included reference occupations selected at a threshold of 0.05 in the CASSCF wave function (merged from calculations on the cyclic and linear forms) as described in Sec. 2 above. However, in an ACPF calculation employing all single and double excitations from this reference space five additional CSFs appear with final ACPF coefficients greater than 0.05. All these CSFs are valence occupations, and so were added to the reference space. Results obtained with this expanded reference space are denoted 0.05e. An ACPF calculation based on the expanded reference space does not show any new CSFs with coefficients greater than 0.05. We also note that at our tighter

selection thresholds of 0.025 and 0.01 no problems with additional references arise.

The 0.05 threshold results for the  $\Delta E$  are all rather large; comparisons with the tighter selection thresholds show several trends. First, the computed  $\Delta E$  decreases on expansion of the reference space. Concomitantly, the effect of the size-consistency correction decreases, and the MRCI+Q and ACPF values approach each other. The latter two effects are readily explained by considering the weight of the reference configurations given in Table II: MRCI(0.05) and especially ACPF(0.05) show large deviations from unity for this quantity. The weight of the reference configurations is considerably smaller for ACPF(0.05) than for MRCI(0.05), but this situation improves with expansion of the reference space.

MRCI calculations have also been carried out in a space of 12 MOs — these are denoted Val(0.05e), etc, since they correspond to valence space calculations. By comparison with the CASSCF results, which represent a full CI in this MO space, it can then be assessed whether the method is capable of a balanced treatment of internal correlation. While the Val(0.05e)  $\Delta E$  differs significantly from the CASSCF result, the MRCI(0.025) and MRCI+Q(0.025) values bracket it. (The Val(0.025) wave function has a sum of squared reference coefficients of about 96%.)

As a final  $n$ -particle calibration step, an MRCI calculation at a reference selection threshold of 0.01 has been performed. The resulting MRCI wave function comprises more than 3.3M CSFs. (As the ACPF(0.025) calculation converged rather slowly, an ACPF(0.01) calculation was not attempted since it would have severely strained our computing resources.) The MRCI(0.01) results further reduce  $\Delta E$  to 1.68 kcal/mol (1.60 kcal/mol without the Davidson correction). The difference between the various size-consistency correction formulas becomes on the order of 0.01 kcal/mol, and is thus negligible. The Val(0.01) results, both for the total energies and the  $\Delta E$ , nearly coincide with the CASSCF values, verifying that the treatment of internal correlation is effectively complete. Table II shows that the reference configurations comprise about 98.5% of the Val(0.01) wave function and about 93.5% of MRCI(0.01).

Most strikingly, the final MRCI+Q(0.01)  $\Delta E$  is very close to the CASSCF result. Hence in this basis set the differential effect (between the two structures) of external correlation is essentially negligible. Of all the single-reference methods in Table I, QCISD(T) is closest to the MRCI+Q(0.01)  $\Delta E$ , whereas CISDTQ appears to seriously overshoot. This again attests to the ability of single-reference coupled-cluster methods to overcome, at least in part, near-degeneracy problems that would otherwise require a multireference treatment. The QCISD(T) total energies, however, differ from the MRCI+Q(0.01)

energies by amounts similar in magnitude to  $\Delta E$ , so some error compensation is certainly involved. Given its very substantial multireference character,  $C_3^+$  should be valuable as a test system for electron correlation methods (see Ref. 20, for example). Our MRCI+Q(0.01) energies should be useful as a comparison standard for this purpose.

### 3.2 One-particle basis set calibration

Carrying out an MRCI(0.01) calculation in the  $[5s3p2d1f]$  basis is considerably beyond our current resources: the wave function would involve well over twenty million CSFs. We have performed calculations at three levels, QCISD(T), CASSCF, and MRCI(0.025) (these calculations employed an  $f$  exponent of 0.966). The MRCI(0.025) calculation is at the limit of our computational capabilities, even with the three highest virtual orbitals excluded from the correlation treatment and only the pure spherical harmonic components of the basis functions retained. The final MRCI wave functions comprise almost six million CSFs. Our results are given in Table III.

Val(0.025) calculations have also been performed, in order to assess the quality of the internal correlation treatment. Once again, the MRCI(0.025) and MRCI+Q(0.025) values bracket the CASSCF  $\Delta E$ . To assess the effect on internal correlation of using Cartesian Gaussians instead of spherical harmonics, a CASSCF result using the former is also reported. The CASSCF total energies are lowered by about 1 mE<sub>h</sub>, and the  $\Delta E$  is increased by less than 0.1 kcal/mol.

It is apparent from a comparison of Tables II and III that expansion of the basis set favors the cyclic form, as expected from the single-reference results. The scatter in the  $\Delta E$  values of Table II (excluding QCISD) is about 2 kcal/mol, with Val(0.025) producing the lowest and the MRCI+Q(0.025) the highest result. If we assume that the difference between the MRCI+Q(0.01) and MRCI+Q(0.025) results in the DZP basis is transferable to the larger basis (this is certainly preferable to making no correction for the effect of the selection threshold) we obtain an estimated  $\Delta E$  of 4.12 kcal/mol, while the same approach applied to the MRCI(0.025) result gives 4.10 kcal/mol. Finally, if we correct the larger basis QCISD(T) result by the difference between the QCISD(T)/DZP and MRCI+Q(0.01)/DZP values we obtain an estimated  $\Delta E$  of 4.23 kcal/mol.

Comparison of Tables I, II, and III gives a direct measurement of the effect of expanding the one-particle basis for given correlation treatments. At the CASSCF, Val(0.025), or Val+Q(0.025) level,  $\Delta E$  increases by 1.7 kcal/mol on going from the  $[4s2p1d]$  to the  $[5s3p2d1f]$  basis. At the MRCI+Q(0.025) or QCISD(T) level, the increase is 2.5 kcal/mol (the increase is almost the same at the MRCI(0.025) level). This implies that the basis



set effect on *dynamical* correlation here is only 0.8 kcal/mol. Using the approach outlined above to correct for *n*-particle space improvements, we expect that the MRCI(0.01) or MRCI+Q(0.01) result in the [5s3p2d1f] basis set would be about 4.2 kcal/mol. This could still be an overestimate of the full CI result in the [5s3p2d1f] basis, since 1 kcal/mol may be an underestimate of the effects of *n*-particle space truncation. The major remaining source of error, however, is undoubtedly the one-particle basis set. Given that non-dynamical correlation is apparently more important than dynamical correlation in determining  $\Delta E$ , the basis set effects computed by Scuseria<sup>20</sup> may be something of an overestimate, but they should certainly supply a good guide to the maximum probable  $\Delta E$ . We therefore assume that basis set saturation could increase  $\Delta E$  by as much as 2.5 kcal/mol, based on Scuseria's CCSD(T) investigation of basis set effects. Even if neglected correlation effects (i.e., beyond MRCI+Q(0.025)) have been underestimated above, it seems very improbable that  $\Delta E$  could be smaller than 4.2 kcal/mol, and it could be as large as 6.7 kcal/mol. Our best estimate, given our computed numbers, is thus  $5.2^{+1.5}_{-1.0}$  kcal/mol.

Our best estimate is 2.2 kcal/mol higher than the QCISD(T)/6-311+G(2df) value computed by Raghavachari, and 3.2 kcal/mol higher than the best estimate of MFG. The *n*-particle calibration accounts for much of the difference with the Raghavachari value, and most of the remainder will be due to basis set differences; there may be some effect from different choices of reference geometry, as illustrated by Table IV, where QCISD(T)/6-31G\* values are tabulated for various reference geometries. The fairly large effect on  $\Delta E$  of using MP2/6-311G\* reference geometries is explained by the fact that although the bond length is close to the QCISD(T)/6-31G\* optimum value, the bond angle differs by about 6 degrees. There is some compensation of errors in bond length and angle in the CISD/TZ2P geometry, leading to a predicted  $\Delta E$  that is in close agreement with the value at the QCISD(T)/6-31G\* optimum geometry. It is also worth noting that the QCISD(T)/6-31G\* geometry reported by Raghavachari is in close agreement with the CASSCF/TZ2P geometry reported by GAS.

Finally, our estimate is smaller than Scuseria's best computed value<sup>20</sup>, although our uncertainty essentially encompasses it. Our [4s2p1d] MRCI(0.01) result is over 1 kcal/mol smaller than his DZP CCSD(T) result<sup>20</sup>, and it seems very likely that the CCSD(T) method overestimates  $\Delta E$  by at least this amount, although part of the difference may be due to the use of different reference geometries. It is interesting to note in passing that while this seems to be a case where CCSD(T) and QCISD(T) disagree, since  $\Delta E$  from the two methods differs by 2 kcal/mol, this probably reflects mainly the fact that

the QCISD(T) treatment is UHF-based, while the CCSD(T) is RHF-based. For example, making the RHF/UHF correction referred to in Section 3.1 halves the difference.

### 3.3 Is linear $C_3^+$ a local minimum or a transition state?

Raghavachari observed that, when the bond distance was kept fixed at 1.32 Å and the bond angle was varied, the QCISD(T)/6-31G\* energy went through a maximum at about 100 degrees. More specifically, the energy at 100 degrees was 4.98 kcal/mol above that at 70 degrees (corresponding to the cyclic structure), and 4.24 kcal/mol above the linear structure. Raghavachari expected the barrier to increase upon enlargement of the basis set, and saw this as indicating that the QCISD(T) treatment was of dubious quality for this molecule. (It should be remembered, however, that this conclusion was based on the erroneous GAS results.)

Given the apparently good performance of the QCISD(T) method, compared to MRCI, for  $C_3^+$ , we are no longer convinced that Raghavachari's doubts were justified. Three explanations can be advanced to explain the double minimum: (a) it is a basis set artifact; (b) it is a correlation method artifact; (c) it is an actual physical feature of the potential surface. Possibility (b) seems remote, in view of our calibration studies above; in order to eliminate (a), we have performed a single QCISD(T)/[5s3p2d1f] calculation at  $r=1.290$  Å,  $\theta=100.0$  degrees. The computed energies are: QCISD  $-113.36132 E_h$ , QCISD(T)  $-113.39867 E_h$ . So there is indeed a double minimum at the QCISD(T) level not seen at the QCISD level, and thus coming from the triple excitations. The energy is 5.29 kcal/mol above that of the cyclic form, but only 1.87 kcal/mol above the linear form. This corresponds to a linear isomer with a large-amplitude very low bending frequency. It is possible that further improvement of basis set and electron correlation treatment would remove the hump, but the actual potential surface may well exhibit a double minimum.

We have also performed CASSCF geometry optimization and harmonic frequency calculation in both the [4s2p1d] and [5s3p2d1f] basis sets, the results of which are summarized in Table V. We note that the use of our optimized CASSCF geometries instead of the GAS CISD structures would have lowered our computed CASSCF  $\Delta E$  above by 0.11 kcal/mol. The linear structure exhibits symmetry breaking at the CASSCF level — this is presumably an artifact arising from the choice of active space, since it occurs in both basis sets. Such symmetry breaking is not uncommon in radicals and was noted for  $C_3^+$  by GAS at the CISD/TZ2P level and by Raghavachari at the QCISD(T)/6-31G\* level. We have located the broken-symmetry solution in the [4s2p1d] basis: a  $^2\Sigma^+$  state

with all frequencies real. Its bending frequency is very low ( $112\text{ cm}^{-1}$ ). Estimating the zero-point energies from these latter frequencies and those for the cyclic form, we find that they will shift the  $\Delta E$  by  $-0.24\text{ kcal/mol}$ , i.e., favoring the linear form. However, there is considerable uncertainty in this zero-point correction given the symmetry breaking for the linear structure. The basis set effect on the CASSCF frequencies is rather small for the cyclic structure, with the largest change being a  $35\text{ cm}^{-1}$  increase in the asymmetric stretch. The one real frequency of the symmetric linear structure is also only slightly increased by expanding the basis set. If we assume that all frequencies of the symmetry-broken linear form would be increased proportionally by this factor, we would obtain an estimated  $[5s3p2d1f]$  zero-point correction of  $-0.29\text{ kcal/mol}$ , but again this result should be viewed with some skepticism. Elementary reasoning suggests that zero-point vibration will favor the linear form, of course, but it is difficult to say by how much with only the results given here.

The  $B_2$  vibration of the cyclic form has a large IR intensity<sup>11</sup>, and could thus in principle be detected experimentally. Our CASSCF/ $[5s3p2d1f]$  value of  $980\text{ cm}^{-1}$  for the harmonic frequency may aid experimentalists in identifying it. This value should normally be a lower bound, as only internal correlation is included, with the QCISD(T)/6-31G\* value of  $1194\text{ cm}^{-1}$  found by Raghavachari serving as an upper bound. The cause of the discrepancy between the GAS CASSCF/TZ2P value of  $1124\text{ cm}^{-1}$  and our present results is not clear.

As an additional aid to experimentalists, we have computed the isotopic substitution shifts for the  $B_2$  vibration from the CASSCF/ $[5s3p2d1f]$  force constant matrix. They are (the middle atom corresponding to the apical one):  $\Delta(13 - 12 - 12) = -12.2$ ,  $\Delta(12 - 13 - 12) = -14.3$ ,  $\Delta(13 - 12 - 13) = -23.9$ , and finally  $\Delta(13 - 13 - 12) = -26.7\text{ cm}^{-1}$ . As shown in Ref. 2 for carbon clusters, such *ab initio* isotope shifts are normally in excellent agreement with the experimental ones if they are scaled by the ratio between the computed and observed frequency, and are thus quite useful in confirming or rejecting an assignment.

One practical implication of the double minimum in the bending coordinate being an actual potential surface feature would be that quasilinear behavior of the  $^2B_2$  state can be completely ruled out at the temperatures involved in the Coulomb explosion experiments<sup>6</sup> (about  $450\text{ K}$ ). Hence the ambiguity pointed out by Vager and Kanter<sup>7</sup> can be resolved in favor of an unambiguous interpretation as a cyclic  $^2B_2$  state. Actually, as the  $^2A_1$  transition state (the other Jahn-Teller component of the equilateral triangular structure) was found by all three previous theoretical studies, GAS, MFG and Raghavachari,

to be lower in energy than the barrier towards the linear state, the effective structure would become  ${}^2E'$  before the molecule starts exhibiting quasilinear behavior, as the temperature is increased. At high temperatures, the two effects will combine to make  $C_3^+$  into one of the most fluxional covalent small molecules known.

## 4 Conclusions

We have definitively shown that the ground state of  $C_3^+$  is a cyclic  ${}^2B_2$  state. The linear  ${}^2\Sigma_u^+$  structure lies  $5.2_{-1.0}^{+1.5}$  kcal/mol higher in energy, and is probably not a transition state but a local minimum. The computed isomerization energy is exceptionally sensitive to the electron correlation treatment, particularly with respect to accounting for connected triple excitations in single-reference-based treatments. From our multireference studies, it appears that non-dynamical correlation effects are more important than dynamical correlation effects in determining  $\Delta E$ . We have confirmed that the wave functions for both the cyclic and linear structures show extreme multireference character. Of all the single-reference treatments considered, CCSD(T) and QCISD(T) appear to agree best with our multireference results. The MRCI+Q(0.01)/[4s2p1d]  $\Delta E$  value, which should be very close to the full CI limit in this basis set, is 1.68 kcal/mol; this result may provide a useful calibration for other electron correlation treatments.

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Table I: Total and relative energies with the  $[4s2p1d]$  basis set for various single-reference electron correlation models

Number of MOs	Method	$^2\Sigma_u^+$ $E_h$	$^2B_2$ $E_h$	$\Delta E$ kcal/mol
12	RHF	-112.89028	-112.92951	24.62
	CISD	-113.04280	-113.05366	6.81
	CISD+Q	-113.06858	-113.06823	-0.22
	CISDTQ	-113.06950	-113.06973	0.14
	full CI	-113.07219	-113.07056	-1.02
	UCISD	-113.04826	-113.05658	5.22
	QCISD	-113.06232	-113.06532	1.88
	QCISD(T)	-113.07382	-113.06979	-2.53
24	CISD	-113.14591	-113.16670	13.05
	CISD+Q	-113.18694	-113.19696	6.29
	CISDTQ	-113.20289	-113.20829	3.39
	QCISD	-113.18517	-113.19596	6.77
	QCISD(T)	-113.21344	-113.21121	-1.40
35	CISD	-113.21383	-113.23692	14.49
	CISD+Q	-113.26488	-113.27775	8.08
	CISDTQ	-113.28696	-113.29354	4.13
	QCISD	-113.26193	-113.27580	8.70
	QCISD(T)	-113.29803	-113.29863	0.38
45	CISD	-113.23245	-113.25745	15.69
	CISD+Q	-113.28563	-113.30054	9.36
	UCISD	-113.23517	-113.25848	14.63
	QCISD	-113.28333	-113.29828	9.38
	QCISD(T)	-113.32258	-113.32397	0.87
	MP4(SDQ)	-113.29109	-113.29259	0.94
	MP4(SDTQ)	-113.35983	-113.32058	-24.63
	CISD	-113.23244	-113.25749	15.72
	CISD+Q	-113.28562	-113.30061	9.41
	(a)	-113.29541	-113.30714	7.36
	(b)	-113.30961	-113.31599	4.00
	(c)	-113.29042	-113.30226	7.43

+Q denotes a Davidson correction <sup>27</sup>

(a) using renormalized Davidson correction <sup>28</sup>

(b) using Davidson-Silver correction <sup>29</sup>

(c) using Pople correction <sup>30</sup>

CISD, CISD+Q, CISDTQ, and full CI value are taken from the GAS erratum <sup>14</sup>; other values are computed in this work.

Table II: Total and relative energies with the  $[4s2p1d]$  basis set for various multireference electron correlation models

Method	${}^2\Sigma_u^+$ $E_h$	${}^2B_2$ $E_h$	$\Delta E$ kcal/mol	${}^2\Sigma_u^+$ %ref	${}^2B_2$ %ref
CASSCF	-113.16869	-113.17101	1.46		
Val(0.05e)	-113.16153	-113.16619	2.93	94.2	93.4
Val+Q(0.05e)	-113.16778	-113.17372	3.73		
Val(0.025)	-113.16650	-113.16838	1.19	96.4	95.8
Val+Q(0.025)	-113.16888	-113.17174	1.79		
Val(0.01)	-113.16817	-113.17027	1.32	98.6	98.4
Val+Q(0.01)	-113.16861	-113.17081	1.38		
MRCI(0.05)	-113.30085	-113.30565	3.01	90.1	89.4
MRCI+Q(0.05)	-113.32562	-113.33345	4.91		
ACPF(0.05)	-113.32624	-113.33596	6.10	87.0	83.7
MRCI(0.05e)	-113.30223	-113.30733	3.20	90.6	90.1
MRCI+Q(0.05e)	-113.32557	-113.33253	4.37		
ACPF(0.05e)	-113.32550	-113.33305	4.74	88.3	87.2
MRCI(0.025)	-113.31107	-113.31346	1.50	92.2	91.8
MRCI+Q(0.025)	-113.32750	-113.33186	2.74		
ACPF(0.025)	-113.32685	-113.33134	2.82	90.7	90.0
MRCI(0.01)	-113.31647	-113.31902	1.60	93.7	93.7
MRCI+Q(0.01)	-113.32775	-113.33043	1.68		

+Q denotes a multireference analog <sup>32</sup> of the Davidson correction <sup>27</sup>

(0.05e) represents the (0.05) reference space augmented with five configurations that have coefficients above 0.05 in the ACPF(0.05) calculation (see text).

%ref is the percentage of the wave function contributed by the reference configurations



Table III: Total and relative energies with the [5s3p2d1f] basis set

Method	${}^2\Sigma_u^+$ $E_h$	${}^2B_2$ $E_h$	$\Delta E$ kcal/mol
CASSCF	-113.19311	-113.19818	3.18
CASSCF <sup>a</sup>	-113.19406	-113.19926	3.27
Val(0.025)	-113.19087	-113.19556	2.94
Val+Q(0.025)	-113.19330	-113.19894	3.54
MRCI(0.025) <sup>b</sup>	-113.38360	-113.38985	3.92
MRCI+Q(0.025) <sup>b</sup>	-113.40633	-113.41459	5.18
QCISD	-113.35484	-113.37495	12.62
QCISD(T)	-113.40164	-113.40709	3.42

+Q denotes a multireference analog <sup>32</sup> of the Davidson correction <sup>27</sup>

<sup>a</sup> Cartesian rather than spherical harmonic basis functions

<sup>b</sup> Three highest virtual orbitals were excluded from the calculation

Table IV: Variation of QCISD(T)/6-31G\* results ( $E_h$ , kcal/mol) with choice of reference geometry ( $\text{\AA}$ , degrees)

Level of theory for reference geometry	$^2\Sigma_u^+$		$^2B_2$			$\Delta E$
	$r_e$	E	$r_e$	$\theta$	E	
UHF/6-31G* <sup>11, 10</sup>	1.282	-113.32364	1.283	71.3	-113.32359	-0.03
CISD/TZ2P <sup>9</sup>	1.283	-113.32376	1.296	71.0	-113.32569	1.21
MP2/6-311G* <sup>11</sup>	1.305	-113.32620	1.330	73.1	-113.32630	0.06
QCISD(T)/6-31G* <sup>10</sup>	1.318	-113.32658	1.333	67.0	-113.32832	1.09

Table V: CASSCF geometries ( $\text{\AA}$ , degrees), harmonic frequencies ( $\text{cm}^{-1}$ ), and zero-point energies (ZPE, kcal/mol) for  $\text{C}_3^+$

State	E(E <sub>h</sub> )	r <sub>1</sub>	r <sub>2</sub>	θ	Harmonic frequencies			ZPE
[4s2p1d] basis set								
<sup>2</sup> B <sub>2</sub>	−113.17879	1.350	1.350	66.4	742( <i>a</i> <sub>1</sub> )	945( <i>b</i> <sub>2</sub> )	1610 ( <i>a</i> <sub>1</sub> )	4.71
<sup>2</sup> Σ <sub>u</sub> <sup>+</sup>	−113.17664	1.330	1.330	180.0	46.5 <i>i</i> (π <sub>u</sub> )	2852 <i>i</i> (σ <sub>u</sub> )	1146 (σ <sub>g</sub> )	1.64
<sup>2</sup> Σ <sup>+</sup>	−113.17850	1.283	1.373	180.0	112(π)	1766(σ)	1136 (σ)	4.47
[5s3p2d1f] basis set								
<sup>2</sup> B <sub>2</sub>	−113.20483	1.331	1.331	66.6	760( <i>a</i> <sub>1</sub> )	980( <i>b</i> <sub>2</sub> )	1612 ( <i>a</i> <sub>1</sub> )	4.79
<sup>2</sup> Σ <sub>u</sub> <sup>+</sup>	−113.19953	1.314	1.314	180.0	107 <i>i</i> (π <sub>u</sub> )	5114 <i>i</i> (σ <sub>u</sub> )	1154(σ <sub>g</sub> )	1.65